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**ORIGINAL  
COMPLETE SPECIFICATION  
STANDARD PATENT**

Application Number:

Lodged:

Invention Title:

RUBBER COMPOSITION FOR TIRE CASINGS BASED ON SILICAS  
CONTAINING A REINFORCING ADDITIVE BASED ON A  
FUNCTIONALIZED POLYORGANOSILOXANE AND ON AN  
ORGANOSILANE COMPOUND

The following statement is a full description of this invention, including the  
best method of performing it known to us :-

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## SPECIFICATION

### BACKGROUND OF THE INVENTION

The present invention relates to new rubber compositions intended for the manufacture of tire casings based on precipitated silicas containing a reinforcing  
5 additive based on a functionalized polyorganosiloxane and an organosilane compound.

Since the economies of fuel and the need to protect the environment have become a priority, it is desirable to produce polymers which have good mechanical  
10 properties and a hysteresis which is as low as possible in order to enable them to be used in the form of rubbery compositions which can be employed for the manufacture of

various semifinished products forming part of the constitution of tire casings, such as, for example, underlinings, calendering or sidewall rubbers or treads and to obtain tires with improved properties, which have in particular a reduced rolling resistance.

Many solutions have been proposed to meet such an objective, consisting especially in modifying, among others, the nature of the diene polymers and copolymers at the end of polymerization by means of coupling or starring or functionalizing agents. All these solutions have concentrated essentially on the use of the modified polymers with carbon black as reinforcing filler with the aim of obtaining a good interaction between the modified polymer and the carbon black. It is known, in general, that in order to obtain optimum reinforcing properties which are imparted by a filler it is appropriate that the latter should be present in the elastomer matrix in a final form which is both as finely divided as possible and distributed as homogeneously as possible. However, such conditions can be achieved only insofar as, on the one hand, the filler has a very good capacity for being incorporated into the matrix during the mixing with the elastomer and for being deaggregated or deagglomerated and for being dispersed homogeneously in the elastomer. The use of white reinforcing fillers, and especially of silica, has been found

inappropriate because of the low level of some properties of such compositions and consequently of some properties of the tires utilizing these compositions.

In addition, for reasons of mutual affinities, silica particles have an unfortunate tendency, in the elastomer matrix, to agglomerate together. These silica/silica interactions have the detrimental consequence of limiting the reinforcing properties to a level which is appreciably lower than that which it would be theoretically possible to attain if all the silica/elastomer interactions capable of being created during the mixing operation were actually obtained.

What is more, the use of silica gives rise to difficulties in processing which are due to the silica/silica interactions which tend, in the raw state (before curing), to increase the consistency of the rubbery compositions and, in any event, to make the processing more difficult than the processing of carbon black.

Finally, the interactions between the silica and the crosslinking system, when the latter is sulfur-based, and the accelerators usually employed in the case of sulfur reduce the rate and efficiency of crosslinking.

In the case of silica-reinforced compositions interest has been revived with the publication of European Patent Application EP-A-0 501 227, which discloses a sulfur-

vulcanizable rubber composition obtained by thermomechanical working of a copolymer of conjugated diene and of an aromatic vinyl compound, prepared by polymerization in solution with 30 to 150 parts by weight, per 100 parts by weight of elastomer, of a particular precipitated silica. The use of such a silica has undoubtedly reduced the difficulties in processing the mixtures containing it, predominantly or otherwise, as reinforcing filler, but the processing of such rubbery compositions nevertheless remains more difficult than the processing of carbon black.

It is known to a person skilled in the art that a coupling or bonding agent which reacts with silica must be employed to create good interactions between the surface of the silica and the elastomer while promoting the dispersion of the silica, and the compositions described in European Patent Application EP-A-0 501 227 are also subject to this need.

One objective of a person skilled in the art consists in improving the processing of the diene rubber compositions including silica as reinforcing filler which are intended for the manufacture of tire casings and, on the other hand, to reduce the quantity of coupling and/or reinforcing agent needed, without degrading the properties of such compositions.

Thus, in Patent US-A 3,350,345 it has been

proposed to employ, in rubber compositions including silica, a hydrolyzable silane and in particular a mercaptosilane as elastomer/silica coupling agent. In Patent Application FR-A-2,094,859 it was subsequently proposed to employ rubber  
5 compositions including silica and a mercaptosilane as coupling agent for the manufacture of tire treads, because of the improved properties exhibited by such compositions. It was rapidly demonstrated and known to a person skilled in the art that mercaptosilanes and in particular  $\gamma$ -mercapto-  
10 propyltrimethoxysilane and  $\gamma$ -mercaptopropyltriethoxysilane were capable of providing the best silica/elastomer coupling properties, but that the industrial use of these coupling agents was not possible because of the high reactivity of the SH functional groups resulting very rapidly, during the  
.5 preparation of a composition in an internal mixer, in premature vulcanizations, also called "scorching", with very high Mooney plasticities and, all things considered, in compositions which were virtually impossible to work and to process on industrial scale.

0 To illustrate this impossibility of employing such coupling agents and the compositions containing them on industrial scale, Patent Application FR-A-2,206,330 and Patent US-A-4,002,594 may be mentioned.

To overcome this disadvantage, in Patent  
5 Application FR-A-2,206,330 it has been proposed to employ as

coupling agent organosilane polysulfides, including bis-3-triethoxysilylpropyl tetrasulfide, which are found to give the best compromise, in the case of silica-filled vulcanizates, in terms of scorch safety, ease of processing and reinforcing power. However, this coupling agent is very costly and must be employed in a relatively large quantity, of the order of 2 to 3 times greater than the quantity of  $\gamma$ -mercaptopropyltrimethoxysilane needed to obtain equivalent coupling property levels.

Consequently, it therefore appears desirable from an economical viewpoint to have the ability to develop on industrial scale silica-reinforced rubber compositions including low contents of reinforcing additives which are as effective as mercaptosilanes, but while avoiding premature scorching and problems in processing which are related to an excessive viscosity of the compositions.

An attempt in this direction was described in Patent US-A-4,474,908 which discloses the use of the mixture of a mercaptosilane and an alkoxysilane as reinforcing additive for a rubber composition.

However, this route is not a satisfactory remedy to the problem of scorching and of processing and, in addition, it is costly.

Another attempt has been described in Japanese Patent Application JP-A-06,248,116, which discloses rubber

compositions intended for the manufacture of tire casings including, as reinforcing filler, a blend of carbon black and of silica surface treated with unfunctionalized silicone oils (generally and usually called PDMS by a person skilled  
5 in the art), as well as a silane as coupling agent. This route does not enable the problem faced by a person skilled in the art to be solved, whether the filler consists of a black/silica dilution or silica alone. In fact, the solution described in this application requires the pretreatment of  
10 the silica with the silicone oil at a high temperature (approximately 250°C) and for an extended period (approximately 1 hour) before it is incorporated into the elastomer and into the coupling agent.

The present invention remedies the problem  
15 presented by the use, in rubber compositions based on at least one elastomer and intended for the manufacture of a tire casing which has improved hysteretic properties and which includes silica as reinforcing filler, of a reinforcing additive consisting of the mixture and/or the  
20 product of in situ reaction of at least one functionalized polyorganosiloxane compound containing, per molecule, at least one functional siloxy unit capable of bonding chemically and/or physically with the surface hydroxyl sites of the silica particles and at least one functionalized  
25 organosilane compound containing, per molecule, at least one



functional group capable of bonding chemically and/or physically with the polyorganosiloxane and/or the hydroxyl sites of the silica particles and at least one other functional group capable of bonding chemically and/or physically to the chains of elastomer(s).

Another object of the invention is the use, for the manufacture of tire casings, of a rubber composition based on at least one elastomer, including silica as reinforcing filler and a reinforcing additive consisting of the mixture and/or the product of in situ reaction of at least one functionalized polyorganosiloxane compound containing, per molecule, at least one functional siloxy unit capable of bonding chemically and/or physically with the surface hydroxyl sites of the silica particles and at least one functionalized organosilane compound containing, per molecule, at least one functional group capable of bonding chemically and/or physically with the polyorganosiloxane and/or the hydroxyl sites of the silica particles and at least one other functional group capable of bonding chemically and/or physically to the chains of elastomer(s).

Another subject-matter of the present invention is semifinished constituents which can be employed in the manufacture of tires, especially of treads, and tires which have an improved rolling resistance, obtained by the use of

a rubber composition according to the invention embodying silica as reinforcing filler.

Another subject-matter of the present invention is a process for improving the hysteretic properties of silica-reinforced rubber compositions intended for the manufacture of tire casings, and of semifinished products for tire casings.

Another subject-matter of the present invention is a tire casing including a rubber composition comprising at least one elastomer, silica as a reinforcing filler and a covering additive, wherein the covering additive consists of at least one functionalized polyorganosiloxane compound containing, per molecule, at least one functional siloxy unit capable of bonding chemically and/or physically with the surface hydroxyl sites present on the silica particles.

Finally, another subject-matter of the present invention is a process making it possible to delay substantially the scorching of diene rubber compositions intended for the manufacture of tire casings and of semifinished products for tire casings during the stages of preparation and processing of said compositions.

The reinforcing additive employed in the rubber compositions in accordance with the invention includes, on the one hand, one or a number of functionalized polyorganosiloxane compound(s) containing, per molecule, one

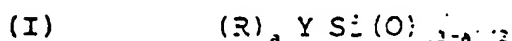
or a number of functional siloxy unit(s) capable of bonding chemically and/or physically with the surface hydroxyl sites of the silica particles and, on the other hand, one or a number of functionalized organosilane compound(s).

- 5 Particularly suitable among the functionalized polyorganosiloxanes are those in which the siloxy units contain a hydrolyzable functional substituent or one or a number of H or OH residue(s) whose reactivity towards silica differs from the other recurring functional substituent(s)
- 10 of the polyorganosiloxane.

Any compound corresponding to any one of the following compounds may be chosen as suitable functionalized polyorganosiloxane compounds for the present invention:

(A) - the compounds containing, per molecule,

- 15 -  $\alpha$  - on the one hand, at least one functional siloxy unit of formula:



in which:

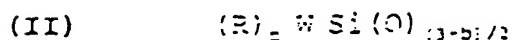
$$a = 0, 1 \text{ or } 2,$$

- 20 R is a monovalent hydrocarbon radical chosen from

linear or branched alkyls containing from 1 to 4 carbon atoms  
 particular methyl, ethyl, propyl and butyl and/or from aryls  
 and in particular phenyl, methyl being more particularly  
 preferred, the radicals R being identical or different when  
 5 a = 2,

Y is a linear or branched alkoxy radical chosen,  
 preferably, from C<sub>1</sub>-C<sub>3</sub>, and in particular C<sub>1</sub>-C<sub>2</sub>, alkoxys,  
 methoxy, ethoxy and (iso)propoxy being more particularly  
 adopted,

10 - β - and optionally, on the other hand, at least one func-  
 tional siloxy unit of formula:



in which:

$$b = 0, 1 \text{ or } 2,$$

15 R corresponds to the same definition as that given  
 above for the substituent R of unit (I) and may be identical  
 with or different from the latter,

W is a monovalent hydrocarbon radical containing  
 from 2 to 30 carbon atoms and optionally S and/or O atoms  
 20 and constituting a functional residue bonded to silicon by

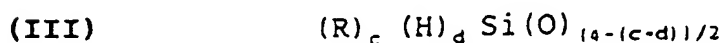
an Si-C bond, this residue being chosen from the following groups:

(i) a linear or branched alkyl group containing at least 7 carbon atoms,

5 (ii) a linear or branched  $C_2-C_{10}$  alkenyl group containing one or more double bond(s) in and/or at the end(s) of the chain(s) said double bonds being preferably conjugated and/or associated with at least one activating group in the  $\alpha$  position,

10 (iii) a saturated or unsaturated aliphatic mono- or polycyclic group containing 5 to 20 carbon atoms and one or more ethylenic double bond(s) in the ring(s), optionally bonded to silicon through the intermediacy of a  $C_2-C_{10}$  linear or branched alkylene radical,

15 -  $\gamma$  - and optionally, on the other hand, at least one siloxy unit of the following formula:



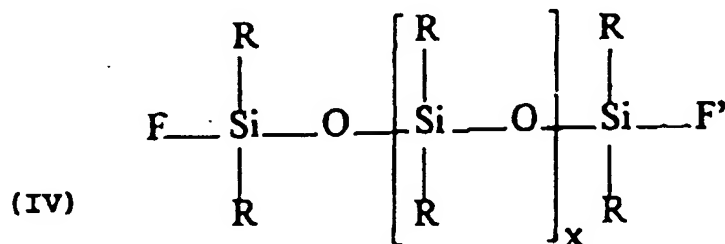
in which:

$$c = 0, 1, 2 \text{ or } 3, \quad d = 1 \text{ and } c + d \leq 3$$

20 the substituents R being as defined above in units (I) and (II).

According to a terminology which is conventional in silicones, the units (I) and (II) may be M, D and T units; in the latter case the polyorganosiloxanes are in the form of linear chains which are mutually crosslinked.

5 (B) - The compounds of formula (IV):



in which:

R is a hydrocarbon radical corresponding to the same definition as that of R given above as legend in  
 0 formula (I), or a linear or branched  $\text{C}_2$ - $\text{C}_{20}$  alkenyl group containing one or more double bonds. The various exemplars of R may be identical with or different from each other,

$x = 0$  to 500, preferably  $x = 0$  to 50,

F and F' are monovalent radicals chosen from  
 5 hydrogen, the halogens and preferably chlorine, those corresponding to the definition of R, and/or hydroxyl,

alkoxy, enoxy, acyloxy, more particularly acetoxy, oxime and amine functional groups; the hydroxyl, methoxy and ethoxy functional groups being more particularly preferred. F and F' may be different or identical, but in the latter case it must not be a question of the radical R, and constitute the functional substituents of the functional siloxy units.

(C) - Polyorganosiloxane resins containing monovalent radicals and/or reactive functional groups F and F', these symbols having the same definition as that given above as legend in formula (IV).

The polyorganosiloxanes (A) are notable in that the functional substituent Y is hydrolyzable and allows grafting on silica, whereas the functional substituent W which is optionally present is hydrolyzable with greater difficulty than the functional substituent Y and is capable of expressing various properties as a function of its chemical nature.

The substituent W of the unit of formula (II) is preferably chosen from the following radicals:

- 20 - a radical (i) containing from 10 to 30 carbon atoms and chosen preferably from the following alkyl radicals:  
dodecyl, undecyl, tridecyl;
- a C<sub>6</sub>-C<sub>10</sub> radical (ii), containing a double bond and preferably another one, conjugated or unconjugated with

the first one;

- a saturated or unsaturated aliphatic monocyclic or polycyclic group (iii) containing 5 to 20 carbon atoms, more particularly cyclohexyl, cyclohexenyl or bicyclic rings originating from norbornene or from dicyclopentadiene, optionally linked to silicon through the intermediacy of a  $C_2-C_6$  linear or branched alkylene radical.

It is appropriate to emphasize that when more than one exemplar of a unit of a given type (I, II or III) is present in the polyorganosiloxane, the various exemplars may be identical with or different from each other. It is even possible advantageously to use this plurality to advantage. For example, functionalized polyorganosiloxanes simultaneously carrying ethoxy and methoxy functional groups as functional groups Y will enable a person skilled in the art to modulate the rate of reaction with the silica as a function of the respective percentages of the two functional groups.

Bearing in mind the values which can be taken by the indices a to d attributed to the substituents in the units (I), (II) and (III), it must be understood that the polyorganosiloxanes may exhibit a linear and/or branched and/or cyclic structure.

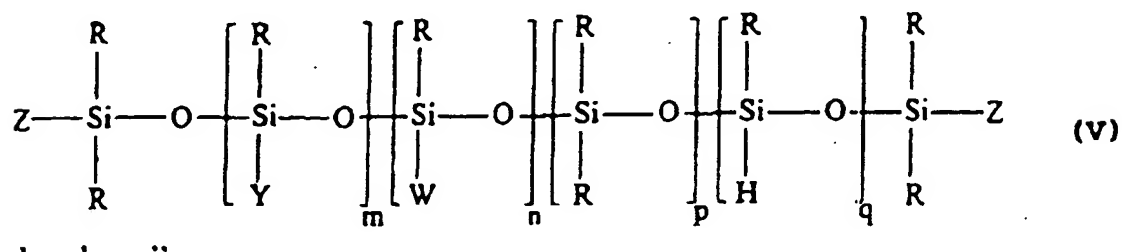
The preferred radicals R are: methyl, ethyl, n-propyl, isopropyl or n-butyl. Still more preferably, at



least 80 % of the number of the radicals R are methyls.

The preferred alkoxy radicals Y are ethoxys.

As preferred polyorganosiloxanes with which the invention is concerned there are mentioned first of all  
 5 those formed by random, sequential or block linear copolymers of the following average formula (V):



in which:

the symbols Y, W and R are as defined above,

the symbol Z is a monovalent radical chosen from  
the radicals formed by hydrogen and from those corresponding  
5 to the definitions of R, Y and W,

the sum  $m + n + p + q \geq 3$ , preferably between 3  
and 100; the illustrated case in which  $p = q = 0$ ,  $m \geq 1$  and  
 $n \leq 50$  being more particularly preferred,

10  $0 \leq m \leq 100$ , preferably  $1 \leq m \leq 50$   
 $0 \leq n \leq 100$ , preferably  $1 \leq n \leq 50$   
 $0 \leq p \leq 20$ , preferably  $0 \leq p \leq 10$   
 $0 \leq q \leq 40$ , preferably  $0 \leq q \leq 10$ ,

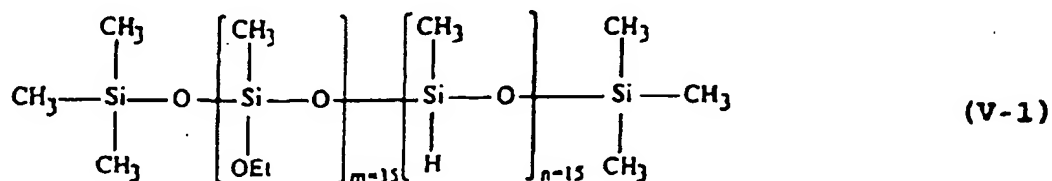
with the conditions according to which:

- if  $m = 0$ , at least one of the substituents Z  
15 corresponds to a radical corresponding to the  
definition characterizing Y
- if  $m = n = 0$  and  $p + q \geq 1$ , then at least one of the  
substituents Z corresponds to a radical corresponding  
to the definition characterizing Y.

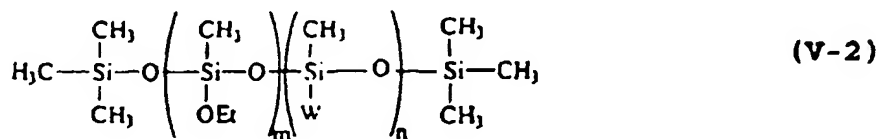
20 Among the polyorganosiloxanes of formula (V) which

are more particularly preferred there may be mentioned those in the case of which  $p = q = 1$  and  $0.5 \leq m/n \leq 5$ , preferably  $1 \leq m/n \leq 3$ .

The compounds corresponding to the following  
5 formulae may be mentioned by way of examples of linear functionalized polyorganosiloxanes:

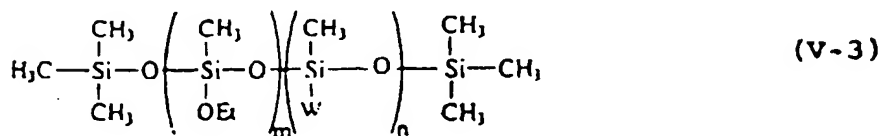


with, on average,  $m: 35$  and  $n: 15$

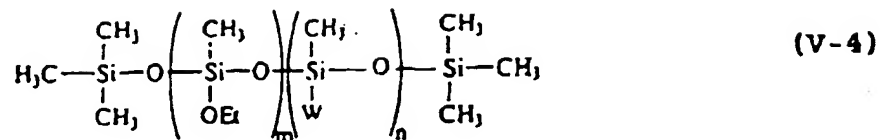


10 with, on average,  $m: 29$  and  $n: 15$  and  $W$  corresponding to:

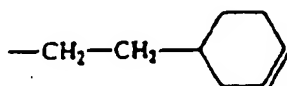
$-(\text{CH}_2)_2$ ,  $-\text{CH}_3$



with, on average, m: 23 and n: 8.5 and W corresponding to: -  
 -(CH<sub>2</sub>)<sub>4</sub>-CH=CH<sub>2</sub>

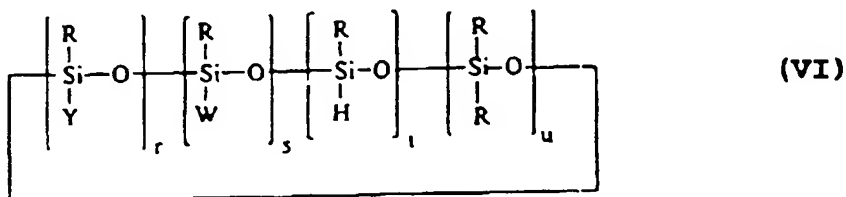


with, on average, m: 35 and n: 16 and W corresponding to:



5

An alternative to the linear structure of the polymers of formula (V) as defined above relates to polyorganosiloxanes consisting of cyclic copolymers of the following average formula:



10 in which:

Y, W and R are as defined above, and with r, s, t and u representing positive whole or decimal numbers,

the sum  $r + s + t + u \geq 3$ , preferably between 4 and 8, the case illustrated in which  $t = u = 0$  being more particularly preferred,

- 5
- $1 \leq r \leq 8$ , preferably  $1 \leq r \leq 4$
  - $1 \leq s \leq 8$ , preferably  $1 \leq s \leq 4$
  - $0 \leq t \leq 8$ , preferably  $0 \leq t \leq 4$
  - $0 \leq u \leq 8$ , preferably  $0 \leq u \leq 4$ .

The polyorganosiloxanes preferably consist of products corresponding to those in the case of which  $R = CH_3$ ,  
10 and  $p = u = 0$  and  $q = t = 0$  in the formulae (V) and (VI) defined above.

It is obvious that, as already indicated above, in these formulae (V) and (VI) the radicals W may be of identical or different nature when  $n > 1$  and  $s > 1$ .

15 A number of polyorganosiloxanes of the type defined above may, of course, be employed within the scope of the present invention.

These polyorganosiloxanes and especially the multifunctional polyorganosiloxanes are obtained according  
20 to a process consisting, on the one hand, in reacting a starting polyorganosiloxane containing units of formula (II) as defined above, in which W denotes hydrogen, with at least one alcohol from which the functionality Y of the unit (I) is derived, and used at the same time as a reactant and as  
25 reaction solvent, in the presence of a catalyst in which at

least one of the active elements is chosen from the transition metals, according to a dehydrocondensation mechanism (1st stage), and, on the other hand, in using the addition of the polyorganosiloxane converted by dehydrocondensation to at least one olefinic compound from which the functionality W of the unit (II) is derived according to a hydrosilylation mechanism (2nd stage), in the presence of a catalyst and preferably at a temperature of between 5 and 100°C and still more preferably between 5 and 70°C.

As a matter of priority, the alcohols used are monohydroxy linear or branched alkanols (primary, secondary or tertiary, preferably primary) which are preferably chosen from the following list: methanol, ethanol, (iso)propanol and (n) butanol, ethanol being preferred.

With regard to the catalyst, this is advantageously chosen from those containing at least one of the following elements: Pt, Rh, Ru, Pd and Ni and their combinations, this catalyst being optionally coupled to a support which is inert or otherwise.

According to a preferred arrangement of the invention, the catalyst is taken from the class of the platinum catalysts which are conventionally employed for carrying out hydrosilylation reactions. These platinum catalysts are extensively described in the literature. It is possible, in particular, to mention the complexes of

platinum and of an organic product which are described in US Patents US-A-3 159 601, US-A-3 159 602, US-A-3 220 972 and European Patents EP-A-57 459, EP-188 978, EP-A-190 530 and the complexes of platinum and of vinylorganopolysiloxane described in US Patents US-A-3 419 593, US-A-3 715 334, US-A-3 377 432 and US-A-3 814 730. The Karstedt catalyst is an example of platinum catalyst which is appropriate for the process according to the invention. (Karstedt patent US-A-3 775 452).

10           Nickel-based catalysts like, for example, Raney nickel, constitute a possible alternative to the platinum catalysts.

Where the reaction conditions are concerned, the dehydrocondensation can be carried out over a wide range of temperature extending, for example, from 0 to 200°C, but it is clear that it is preferred that it should be performed at a temperature of between 10 and 50°C, preferably between 18 and 35°C.

20           The second stage of the process according to the invention consists of a reaction of addition of the hydrogenated intermediate polyorganosiloxane produced by dehydrocondensation to at least one olefinic compound carrying at least one  $\pi$  bond.

25           This involves a hydrosilylation mechanism, in the presence of a catalyst and, preferably, at a temperature

between 5 and 100°C and still more preferably between 5 and 70°C.

According to a preferred methodology the hydrosilylation is initiated by adding the olefinic compound from which the radical W as defined above is derived to the intermediate alkoxyated polyorganosiloxane, once the dehydrocondensation is finished. In practice this addition can take place when the release of hydrogen has ceased.

The reactive alkene may be formed by a mixture of products comprising a single or a number of precursor species of radicals W, which determine the multifunctionality of the final polyorganosiloxane. In the case where a number of species W are provided, the alkene corresponding to the second functionality is preferably allowed to react first of all and then, once the latter has reacted completely, the alkene corresponding to the third functionality is incorporated, and so on.

Instead of being incorporated into the reaction mixture after dehydrocondensation, the olefinic compound which is a precursor of W may be used before this first stage of the process begins, or else during it.

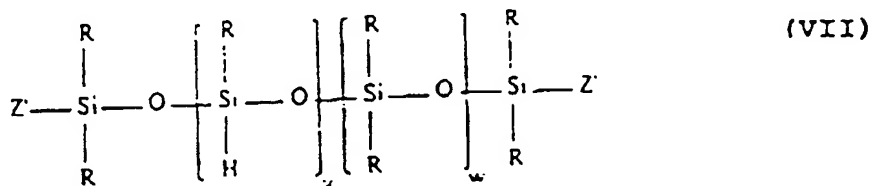
The olefinic compounds used can be easily deduced from the definition of W given above. The choice with regard to this radical is determined by the intended applications (one or a number of different functionalities).



The hydrosilylation stage may advantageously take place at ambient temperature and in bulk or in solution, for example in the alcohol which has been used as solvent for the dehydrocondensation reaction.

5 When the reactions are finished, the raw polyorganosiloxanes which are obtained may be purified particularly by being passed through a column filled with an ion exchange resin and/or by simple devolatilization of the excess reactants introduced and optionally of the solvent  
10 used, by heating which is performed between 100 and 180°C at reduced pressure.

The starting polyorganosiloxane is advantageously selected from those corresponding to the following formula:



15 in which:

the symbols R are identical or different and are as defined above as legend to the formula of units (I) and (II).

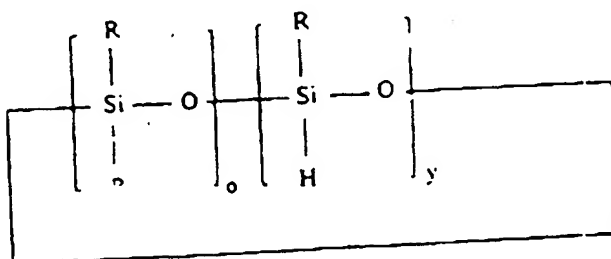
the symbols  $Z'$  are identical or different and correspond to R or to hydrogen,

$v$  is an integer or a decimal number  $\geq 0$  which can be defined as follows:  $v = n + m + p$ ;  $n$ ,  $m$  and  $p$

- 5 corresponding to the definitions given above as legend to the formula of unit (V), with the condition according to which if  $v = 0$  then  $w \geq 1$  and both radicals  $Z'$  correspond to hydrogen,

- 10  $w$  corresponds to the same definition as that of  $p$  given above as legend to the formula of unit (V).

The starting polyorganosiloxanes used, for example, for the preparation of the cyclic functionalized products are those selected from those corresponding to the following average formula:



(VIII)

15

in which:

the symbols R are identical or different and are as defined above, as legend to the formula of units (I) and (II),

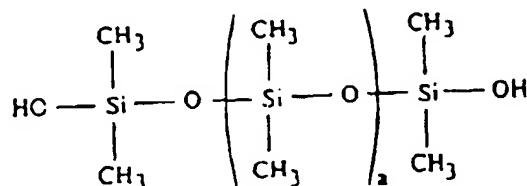
5 o corresponds to the same definition as that of u given above, as legend to the formula of unit (VI),

y is an integer or a decimal number  $\geq 0$ , which can be defined as follows:  $y = r + s + t$  and  $y + u \geq 3$ ; r, s, t and u corresponding to the definitions given above as legend  
0 to the formula of unit (VI).

The following are preferably suitable as examples of compounds (B):

The silanol-ended polydimethylsiloxanes such as the following commercial products manufactured by Huls  
5 America Inc. which appear in the 1994 catalog of the company ABCR - Roth - Sochiel Sarl under the reference:

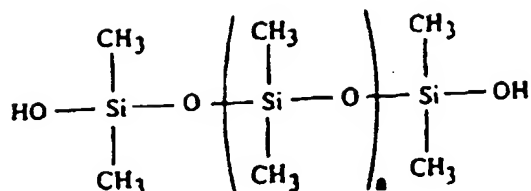
PS 340



with a denoting a positive integer, to give a

weight-average mass between 400 and 700.

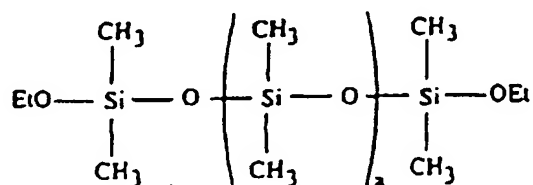
PS 341



with a denoting a positive integer, to give a weight-average mass of 4200.

- 5 The polydimethylsiloxanes ending in ethoxy groups, such as the products manufactured by Huls America Inc. and which appear in the 1994 catalog of the company ABCR - Roth-Sochiel Sarl under the reference:

PS 395

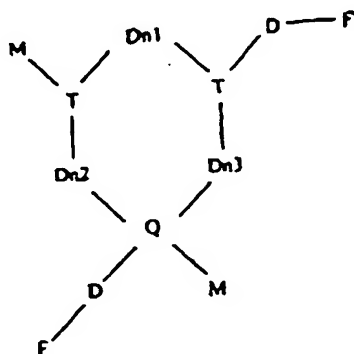


- 10 with a denoting a positive integer, to give a weight-average mass between 700 and 1200.

The compounds (C) are polyorganosiloxane resins consisting of small macromolecular networks of one or more ring(s) as a result of the presence of M, D, T or Q units in

the molecule, according to a conventional silicone terminology, and containing monovalent radicals and/or reactive functional groups.

By way of example of such resins there may be mentioned the compounds corresponding to the formula:



(IX)

in which:

$n$  denotes the number of D units in each chain link of the ring:  $0 \leq n_1, n_2, n_3 \leq 20$

10 F and F' are monovalent radicals chosen from hydrogen, chlorine, those corresponding to the definition of R, and/or hydroxyl, alkoxy, enoxy, acyloxy, more particularly acetoxy, oxime and amine functional groups; the hydroxyl, methoxy and ethoxy functional groups being more

particularly preferred; F and F' may be different or identical, but in the latter case it must not be the radical R.

It is obvious that the number of chain links of each ring may be greater than 3, just as the number of units F may be greater than 2, while being of the same kind or of different kinds.

By way of example of such resins there may be mentioned the MQ resins, the MDQ resins, the DT resins and the MDT resins, which have a hydroxyl or alkyl group weight content of between 1 and 6%.

More particularly, the resins which have a molecular mass lower than 25,000 may be employed.

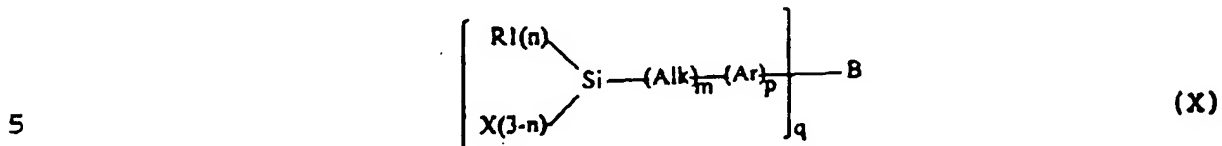
By way of preferred example of compounds (C) there may be mentioned the polyorganosiloxane resin 4509 marketed by the company Rhône-Poulenc, in which the molar percentage of the various units M, D and T is:

M = 15%, D = 25%, T = 60%

and the percentage, by volume, of hydroxyl functional groups = 0.5%.

Finally, it is possible within the scope of the invention to employ a mixture of at least two of the polyorganosiloxanes A, B and C.

One or more compounds corresponding to at least one of the following four general formulae (X) to (XIII) are suitable as organosilane compounds which can be employed within the scope of the invention:



in which:

R1 denotes an alkyl group containing 1 to 10 carbon atoms, or else the phenyl radical,

X denotes a hydrolyzable group chosen from:

- 0
- the halogens, preferably chlorine,
  - alkoxy or cycloalkoxy radicals,
  - acyloxy radicals,

after hydrolysis, X may optionally denote a hydroxyl group (OH).

5

$$0 \leq n \leq 2$$

(Alk) denotes a divalent hydrocarbon group chosen from linear or branched alkyls containing from 1 to 10

carbon atoms and advantageously from 1 to 6,

m denotes 0 or 1,

(Ar) denotes a hydrocarbon group chosen from aryls, containing from 6 to 12 carbon atoms and preferably 6 to 8,

p denotes 0 or 1, with the condition that p and m are not equal to 0 simultaneously,

q = 1 or 2,

B denotes a group capable of forming a bond with at least one of the elastomers of the rubber composition. The preferred groups B are the mercapto (SH) groups in the case of q = 1 and the polysulfide (S<sub>x</sub>) and disulfide (S<sub>2</sub>) groups in the case of q = 2.

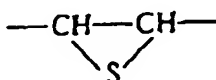
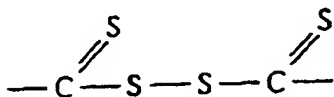
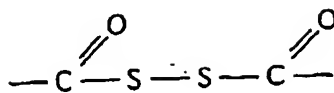
However, the group B may also include other groups capable of reaction with the rubbery polymer, for example:

B denotes:

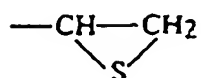
- if q = 2: a polysulfured functional group chosen from the following groups:



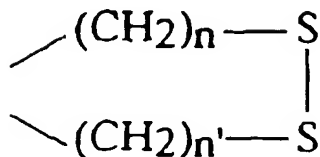
-S<sub>x</sub>- with  $1 \leq x \leq 8$ , x being a positive integer



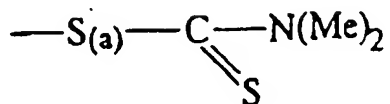
- if  $q = 1$ : a functional group chosen from the following groups:



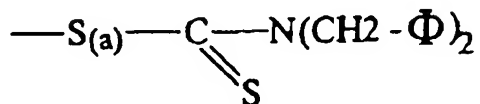
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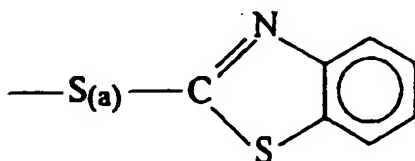
with  $1 \leq n$ ,  $n' \leq 6$  and n can be equal to n'



with  $1 \leq a \leq 8$



with  $1 \leq a \leq 8$

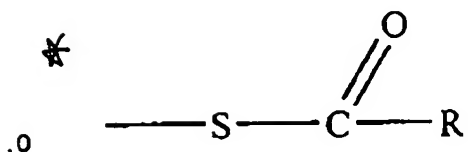


with  $1 \leq a \leq 8$



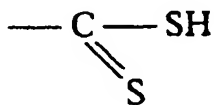
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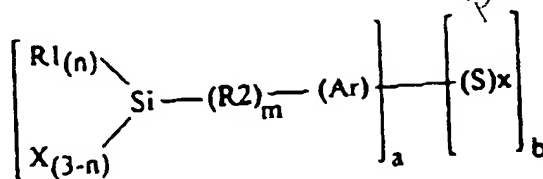
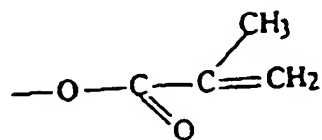
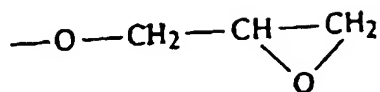
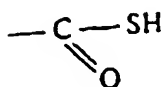
with Z being a halogen residue  
and preferably chloride or  
bromide or a nitrogen  
function, preferably amine or  
amide



10

R: cyclic or acyclic alkyl or  
alkenyl, and aryl





*Polysulfide*

(XI)

in which:

R1 and X correspond to the same definition as that given above as legend to formula (X),

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$$0 \leq n \leq 2,$$

(R2) denotes a divalent hydrocarbon group chosen from linear or branched alkyls and alkylenoxys, containing from 1 to 10 carbon atoms and advantageously from 1 to 6,

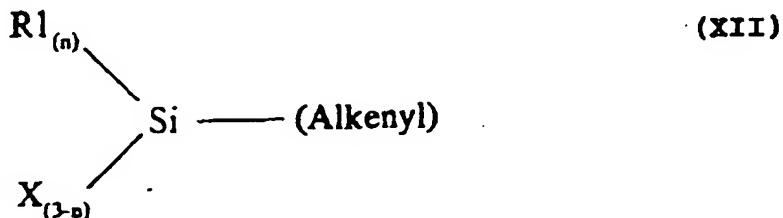
m denotes 0 or 1,

(Ar) denotes a hydrocarbon group chosen from aryls, containing from 6 to 12 carbon atoms,

(S)<sub>x</sub> is a divalent polysulfide radical, each free valency being bonded directly to a carbon atom of an aromatic ring, it being possible for a number of aromatic rings to be linked together by the radical (S)<sub>x</sub>.

$$2 \leq x \leq 6,$$

$$a \geq 2 \text{ and } b \geq 1 \text{ with } 0.4 \leq a/b \leq 2$$



0 in which:

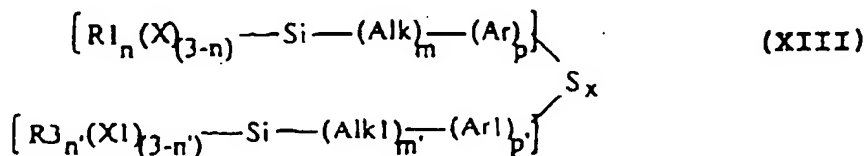
R1 and X correspond to the same definition as that given above as legend to formula (X),

$$0 \leq n \leq 2,$$

Alkenyl denotes a linear or branched hydrocarbon group, cyclic or otherwise, containing one or more double bonds, containing from 2 to 20 carbon atoms and preferably

from 2 to 6. The double bonds are preferably conjugated and/or associated at least with an activating group situated in the  $\alpha$  position.

This class of bonding agent corresponding to the formula (XII) is preferably employed in rubber compositions with at least one radical initiator, preferably consisting of at least one peroxide.



in which:

the symbols  $R1$ ,  $R3$ ,  $X$ ,  $X1$ ,  $Alk$ ,  $Alk1$ ,  $n$ ,  $n'$ ,  $m$ ,  $m'$ ,  $Ar$ ,  $Ar1$ ,  $p$  and  $p'$  are identical or different and correspond to the same definition as that given above as legend to formula (X),

$1 \leq x \leq 8$ ,  $S_x$  therefore denotes a mono-, di- or polysulfide radical,

with the condition of not simultaneously having  $n = n'$ ,  $m = m'$ ,  $p = p'$ ,  $X = X1$ ,  $R1 = R3$ ,  $Alk = Alk1$  and  $Ar = Ar1$ .

Examples of commercial organosilane compounds are given in the table below. Of course, the invention is not limited to these compounds.

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10

Chemical name	Formula	Trade name/supplier
3-Mercaptopropyltrimethoxysilane	HS(CH <sub>2</sub> ) <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	A-139/OSI
3-Mercaptopropyltriethoxysilane	HS(CH <sub>2</sub> ) <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	Dynasylan 3201/Huls
Vinyltriethoxysilane	C <sub>2</sub> H <sub>5</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	Dynasylan VT50/Huls
3-Aminopropyltriethoxysilane	NH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	A-1100/OSI
3-Methacryloxypropyltrimethoxysilane	CH <sub>2</sub> CCH <sub>3</sub> COO(CH <sub>2</sub> ) <sub>3</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	A-174/OSI
Mercaptomethyldimethylethoxysilane	HSC <sub>2</sub> H <sub>4</sub> Si(CH <sub>3</sub> ) <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	M8200/ABC2
Bis(triethoxysilylpropyl) tetrasulfide	[(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> S] <sub>2</sub>	Si 69/Degussa
Bis(trimethoxysilylpropyl) tetrasulfide	[(CH <sub>3</sub> O) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> S] <sub>2</sub>	Si 167/Degussa
3-Chloropropyltrimethoxysilane	(CH <sub>3</sub> O) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> Cl	Si 130/Degussa
3-Thiocyanatopropyltriethoxysilane	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> SCN	Si 264/Degussa
Bis(triethoxysilyl-ethyltolyl) trisulfide	[(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )] <sub>3</sub> S	TRC2/OSI